



### **VERIFICATION OF TRANSLATION**

I, Yoko TANAKA of a member of the technical staff of Miyoshi and Miyoshi, Japan,  
hereby state that I am fluent in the English language and in the Japanese  
language. I hereby verify that the attached English language translation of the  
Japanese language patent application for P2000-313720, filed on October 13, 2000,  
and entitled

**"INCOMBUSTIBLE RESIN COMPOSITION, AND PREPREG,  
LAMINATED PLATE, METAL-CLAD LAMINATED PLATE PRINTED WIRING  
BOARD AND MULTILAYER PRINTED WIRING BOARD BY USE OF THE SAME"**

to be a true and complete translation to the best of my knowledge and belief.

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By:   
Yoko TANAKA

Translation of Japanese Priority Application "P2000-313720"

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[Title of the Invention] INCOMBUSTIBLE RESIN COMPOSITION, AND  
PREPREG, LAMINATED PLATE, METAL-CLAD LAMINATED PLATE PRINTED  
WIRING BOARD AND MULTILAYER PRINTED WIRING BOARD BY USE OF THE  
SAME

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[NAME OF THE DOCUMENT] SPECIFICATION

[TITLE OF THE INVENTION] INCOMBUSTIBLE RESIN COMPOSITION, AND PREPREG, LAMINATED PLATE, METAL-CLAD LAMINATED PLATE, PRINTED WIRING BOARD AND MULTILAYER PRINTED WIRING BOARD BY USE OF THE SAME

[CLAIM FOR A PATENT]

[Claim 1] An incombustible resin composition, which comprises a silicone polymer, a metal hydrate and a resin material as essential components, wherein the metal hydrate is 20% by weight or more in the total solids of the resin composition.

[Claim 2] The incombustible resin composition according to Claim 1, containing at least a type of resin material which is selected from a group consisting of an epoxy resin, a polyimide resin, a triazine resin, a phenol resin, a melamine resin and denatured resins denaturing these resins.

[Claim 3] The incombustible resin composition according to Claim 1 or 2, wherein the metal hydrate has a surface processed with a silicone polymer.

[Claim 4] The incombustible resin composition according to any one of Claims 1 to 3, wherein the composition is obtained by mixing a processing solution containing the silicone polymer, with the metal hydrate, and then adding a resin compound.

[Claim 5] The incombustible resin composition according to any one of Claims 1 to 4, wherein the metal hydrate includes an aluminum hydroxide.

[Claim 6] The incombustible resin composition according to any one of Claims 1 to 4, wherein the aluminium hydroxide is used as the metal hydrate.

[Claim 7] The incombustible resin composition according to Claim 5 or 6, wherein the aluminium hydroxide has an average particle diameter of 5  $\mu\text{m}$  or less.

[Claim 8] The incombustible resin composition according to any one of Claims 1 to 4, wherein the metal hydrate includes a magnesium hydroxide.

[Claim 9] The incombustible resin composition according to any one of Claims 1 to 4, wherein the metal hydrate includes a calcium hydroxide.

[Claim 10] The incombustible resin composition according to any one of Claims 1 to 9, wherein an end of the silicone polymer has a silanol group capable of reacting with the surface of a metal hydrate.

[Claim 11] The incombustible resin composition according to any one of Claims 1 to 10, wherein a degree of polymerization of the silicone oligomer is in the range of 2 to 100.

[Claim 12] The incombustible resin composition according to Claims 1 to 11, wherein the silicone polymer has an aromatic group.

[Claim 13] The incombustible resin composition according to Claims 1 to 11, wherein each siloxane unit of the silicone polymer has at least one aromatic group, respectively.

[Claim 14] A prepreg manufactured by using the incombustible resin composition according to any one of Claims 1 to 13.

[Claim 15] A laminated plate manufactured by using the prepreg according to Claim 14.

[Claim 16] A metal-clad laminated plate manufactured by using the prepreg according to Claim 14.

[Claim 17] A printed wiring board manufactured by using the laminated plate according to Claim 15, or the metal-clad laminated plate according to Claim 16.

[Claim 18] A multiplayer printed wiring board manufactured by using the prepreg according to Claim 14, the laminated plate according to Claim 15, the metal-clad laminated plate according to Claim 16, or the printed wiring board according to Claim 17.

[DETAILED DESCRIPTION OF THE INVENTION]

[0001]

[Field of the Invention]

The present invention relates to an incombustible resin composition, and a prepreg, a laminated plate, a metal-clad laminated plate, a printed wiring board and a multiplayer printed wiring board using the same, which are suitably used

for a variety of electronic materials.

[0002]

[Prior Art]

Upon most of resin compositions used for a variety of electronic devices, incombustibility is conferred in order to secure the safety involving with fire. In order to make the resin compositions incombustible, a variety of methods have been employed, and bromine compounds have been so far widely used because of their excellent incombustibility. While, people become highly conscious about the environmental destructive problems on a global scale, incombustible systems is examined in place of bromine compounds that has a possibility to form highly toxic compounds, in addition to bromine that is corrosive at the time of burning. On the other hand, as a soldering material of mounted parts, conventionally, Sn-Pb based soldering materials have been mainly used. Since these may pollute the soil at the time of processing disposables, a soldering material without using Pb is considered. When analyzing the reports concerned with soldering materials free from Pb, it is expected that the melting point rises, and therefore it is conceivable that the reflow temperature would also rise.

Under such circumstances, for resin compositions used for electronic materials from now on, where bromine compounds are not used, and at the same time, a higher heat-resistance than those of resin compositions made so far is required.

[0003]

As a method of making materials incombustible in place of bromine compounds, conventionally, an addition of phosphorous and nitrogenous compounds and an introduction of these into the resin skeletons have been performed (Japanese Patent Application Laid-Open No. Hei 11-124489 and Japanese Patent Application Laid-Open No. Hei 11-199753). However, in order to secure the incombustibility using phosphorus and nitrogen, these are required to some extent to be blended. However, when these are blended, there have been problems such

as the increase in the water absorption rate, the decrease in heat resistance, and the like occur. For this reason, for the purpose of reducing the volume of introduction of phosphorus and nitrogen, there is a method of using metal hydrates. For example, Japanese Application laid-Open No. Hei 11-181243 discloses incombustible technique using hydrated alumina. However, since metal hydrates trap water having the cooling effect at the time of burning, there has been a problem that when the volumes of these are blended to some extent, the heat resistance is rapidly lowered.

[0004]

[Problems to be Solved by the Invention]

The reason is that the temperature at which the metal hydrates release water is lower than the melting temperature of the soldering. This tendency is considered to be more significant in the case of the soldering being free from Pb whose melting temperature is expected to rise to a higher point. As a method of enhancing the heat resistance using metal hydrates, a method of using a magnesium hydroxide whose temperatures of releasing water are comparatively high (approximately 340°) has been disclosed (Japanese Patent Application Laid-Open No. Hei 11-181305). However, there has been a problem that a magnesium hydroxide is inferior from the viewpoint of the acid resistance. Moreover, a method of performing silane processing with silane compound monomer to the surface of the metal hydrate for the purpose of enhancing a dispersion of the metal hydrate, the tensile strength, the elongation has been disclosed (Japanese Patent Application Laid-Open No. Hei 11-181305 and Japanese Patent Application Laid-Open No. Hei 11-217467). However, as for the silane compound monomer, the enhancement of the heat resistance of the metal hydrate was not recognized because it is also accompanied with the facts that the heat resistance of the monomer itself is low and the processing efficiency to the surface of the metal hydrate is low. The present invention solves the problems, and the present invention provides an incombustible resin composition, a laminated plate and a

printed wiring board using the same, where the bromine compounds are not required.

[0005]

[Means for Solving the Problems]

The present invention relates to the following:

- (1) An incombustible resin composition, which comprises a silicone polymer, a metal hydrate and a resin material as essential components, wherein the metal hydrate is 20% by weight or more in the total solids of the resin composition.
- (2) The incombustible resin composition according to (1), containing at least a type of resin material which is selected from a group consisting of an epoxy resin, a polyimide resin, a triazine resin, a phenol resin, a melamine resin and denatured resins denaturing these resins.
- (3) The incombustible resin composition according to (1) or (2), wherein the metal hydrate has a surface processed with a silicone polymer.
- (4) The incombustible resin composition according to any one of (1) to (3), wherein the composition is obtained by by mixing a processing solution containing the silicone polymer, with the metal hydrate, and then adding a resin compound.
- (5) The incombustible resin composition according to any one of (1) to (4), wherein the metal hydrate includes an aluminum hydroxide.
- (6) The incombustible resin composition according to any one of (1) to (4), wherein the aluminum hydroxide is used as the metal hydrate.
- (7) The incombustible resin composition according to (5) or (6), wherein the aluminium hydroxide has an average particle diameter of 5  $\mu\text{m}$  or less.
- (8) The incombustible resin composition according to any one of (1) to (4), wherein the metal hydrate includes a magnesium hydroxide.
- (9) The incombustible resin composition according to any one of (1) to (4), wherein the metal hydrate includes a calcium hydroxide.



(10) The incombustible resin composition according to any one of (1) to (9), wherein an end of the silicone polymer has a silanol group capable of reacting with the surface of a metal hydrate.

(11) The incombustible resin composition according to any one of (1) to (10), wherein a degree of polymerization of the silicone oligomer is in the range of 2 to 100.

(12) The incombustible resin composition according to (1) to (11), wherein the silicone polymer has an aromatic group.

(13) The incombustible resin composition according to (1) to (11), wherein each siloxane unit of the silicone polymer has at least one aromatic group, respectively.

(14) A prepreg manufactured by using the incombustible resin composition according to any one of (1) to (13).

(15) A laminated plate manufactured by using the prepreg according to (14).

(16) A metal-clad laminated plate manufactured by using the prepreg according to (14).

(17) A printed wiring board manufactured by using the laminated plate according to (15), or the metal-clad laminated plate according to (16).

(18) A multiplayer printed wiring board manufactured by using the prepreg according to (14), the laminated plate according to (15), the metal-clad laminated plate according to (16), or the printed wiring board according to (17).

[0006]

#### [EMBODIMENTS of the Present Invention]

The present invention relates to an incombustible resin composition, and a laminated plate, a printed wiring board using the composition containing a metal hydrate and a silicone polymer but not containing bromine compounds. Hereinafter, the present invention will be described below.

[0007]

A metal hydrate for use in the invention includes, but not limited to aluminum hydroxide, magnesium hydroxide and calcium hydroxide which are conventionally used in

incombustible resin compositions and known. Considering that the heat resistance, incombustibility and dispersion property of particles are superior, it is preferable that an average particle diameter of the metal hydroxide is 10  $\mu\text{m}$  or less. Moreover, if aluminium hydroxide is used as a metal hydrate, it is particularly preferable to use aluminium hydroxide whose average diameter of the particle is 5  $\mu\text{m}$  or less since its temperature of releasing water and the heat resistance are high. Moreover, these metal hydrates and the other inorganic fillers can be used in combination. The kinds and shapes of inorganic fillers which are used in combination with the metal hydrates are not particularly limited, for example, calcium carbonate, alumina, titanium oxide, mica, aluminium carbonate, magnesium silicate, aluminium silicate, silica and a variety of kinds of whiskers such as glass short fibers, aluminium borate and silicon carbide are used. Furthermore, a few kinds of these may be used in combination. A total blending volume of the metal hydrate and the other inorganic fillers is preferably 20 to 80% by weight with respect to the total solids of the resin composition. Among these, the metal hydrate is 20% by weight or more with respect to the total solids of the resin composition. Incidentally, in the blending volume of the resin composition of the present invention, a volume of each compound is calculated by weight and specific gravity, respectively.

[0008]

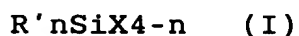
A silicone polymer in the present invention contains at least one kind of siloxane unit selected from bifunctional siloxane unit ( $\text{R}_2\text{SiO}_{2/2}$ ), trifunctional siloxane unit ( $\text{RSiO}_{3/2}$ ) (in the formula, R represents an organic group, R groups in the silicone oligomet may be identical with each other or different.), and tetrafunctional siloxane unit ( $\text{SiO}_{4/2}$ ). Moreover, the silicone polymer has one functional group or more which reacts with hydroxyl group at the end of it. It is preferable that the degree of polymerization is 2 to 7000, more preferably 2 to 100, particularly preferable the degree of polymerization is 2 to 70. Here, the degree of the

polymerization is calculated from the number average molecular weight measured by utilizing calibration curve of the standard polystyrene or polyethylene glycol by its polymer molecular weight (in the case of low degree of polymerization) or gel permeation chromatography. As the R, an alkyl group having 1 to 4 pieces of carbon atoms or an aromatic group such as phenyl group is preferably selected. However, in order to further enhance the heat resistance, it is more preferable that the ratio of aromatic groups is raised. It is particularly preferable that the respective siloxane unit of the silicone polymer contains one aromatic group or more, respectively, and it is particularly preferable that it contains phenyl group. As the functional group reacting with hydroxyl group, silanol group, alkoxyl group having 1 to 4 pieces of carbon atoms, acyloxy group having 1 to 4 pieces of carbon atoms, halogen such as chlorine or the like except for bromine are listed.

[0009]

A silicone polymer of the invention can be obtained by hydrolyzing and performing the polycondensation of silane compound represented by the following general formula (I).

[Formula 1]



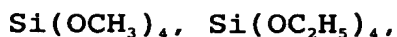
(In the formula, X represents halogen such as chlorine except for bromine, or -OR, where R represents alkyl group having 1 to 4 pieces of carbon atoms or alkyl carbonyl group having 1 to 4 pieces of carbon atoms, R' represents organic groups such as alkyl group having 1 to 4 pieces of carbon atoms or phenyl group, n denotes an integer of 0 to 2).

[0010]

Silane compounds represented by the general formula (I) are concretely,

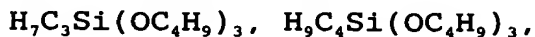
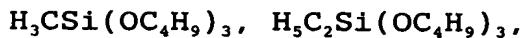
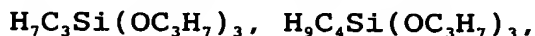
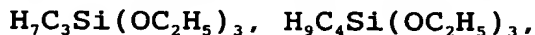
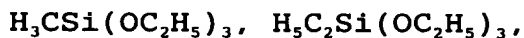
4 functionality silane compounds (hereinafter functionality in the silane compound means that it has functional group having condensation reaction) such as tetraalkoxy silanes as follows:

[Formula 2]



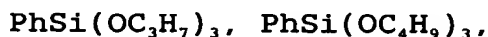
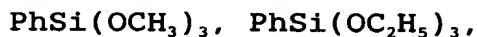
monoalkyl trialkoxy silanes as follows:

[Formula 3]



phenyl trialkoxy silanes as follows:

[Formula 4]



(where Ph represents phenyl group. Hereinafter, referred to as the same as it is represented.)

monoalkyl triacyloxy silanes as follows:

[Formula 5]



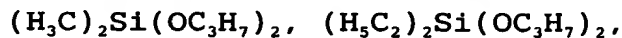
trifunctional silane compounds such as monoalkyl trihalogeno silanes as follows:

[Formula 6]



Dialkyl dialkoxy silanes as follows:

[Formula 7]



$(\text{H}_7\text{C}_3)_2\text{Si}(\text{OC}_4\text{H}_9)_2$ ,  $(\text{H}_9\text{C}_4)_2\text{Si}(\text{OC}_4\text{H}_9)_2$ ,  
diphenyl dialkoxy silanes as follows:

[Formula 8]

$\text{Ph}_2\text{Si}(\text{OCH}_3)_2$ ,  $\text{Ph}_2\text{Si}(\text{OC}_2\text{H}_5)_2$ ,  
Dialkyl dialkoxy silanes as follows:

[Formula 9]

$(\text{H}_3\text{CCOO})_2\text{Si}(\text{CH}_3)_2$ ,  $(\text{H}_3\text{CCOO})_2\text{Si}(\text{C}_2\text{H}_5)_2$ ,  
 $(\text{H}_3\text{CCOO})_2\text{Si}(\text{C}_3\text{H}_7)_2$ ,  $(\text{H}_3\text{CCOO})_2\text{Si}(\text{C}_4\text{H}_9)_2$ , and  
bifunctional silane compounds such as alkyl dihalogeno silanes  
as follows:

[Formula 10]

$\text{Cl}_2\text{Si}(\text{CH}_3)_2$ ,  $\text{Cl}_2\text{Si}(\text{C}_2\text{H}_5)_2$ ,  
 $\text{Cl}_2\text{Si}(\text{C}_3\text{H}_7)_2$ ,  $\text{Cl}_2\text{Si}(\text{C}_4\text{H}_9)_2$ .

[0011]

As a silane compound represented by the general formula (I) of the present invention, any of tetrafunctional silane compound, trifunctional silane compound, bifunctional silane compound or their mixture is appropriately used. In order to enhance the heat resistance, it is preferable to use silane compound having an aromatic group. It is particularly preferable to use phenyl trialkoxy silane compound having a phenyl group and diphenyl dialkoxy silane compound. As a usage volume of the compound having a phenyl group, it is preferable that it is used at the ratio of 5 to 100 mol% with respect to the total silane compound. It is particularly preferable to use it at the ratio of 50 to 100 mol%.

[0012]

A silicone polymer in the present invention is manufactured by hydrolyzing and performing the polycondensation of silane compound represented by the general formula (I). As a catalyst used at this time, it is preferable that: inorganic acids such as hydrochloric acid, sulfuric acid, phosphoric acid, nitric acid and fluoric acid; and organic acids such as oxalic acid, maleic acid, sulfonic acid and formic acid, but basic catalysts such as ammonia and trimethyl ammonium can be also utilized. As to these catalysts, the appropriate volume

is used according to the volume of the silane compound represented by the general formula (I). However, it is preferable used in the range of 0.001 to 1.0 mole with respect to 1 mole of the silane compound represented by the general formula (I).

[0013]

Moreover, at the time of this reaction, water exists. The volume of water is also appropriately determined. If water is too much, the conservation stability of a coating liquid will be lowered. Therefore, as for the volume of water, it is preferably 0 to 5 moles with respect to 1 mole of hydrolytic group (for example, alkoxyl group) that the silane compound represented by the general formula (I) has. It is more preferably in the range of 0.5 to 2 moles.

[0014]

Moreover, it is preferable that the above-described hydrolysis and polycondensation are performed in a solvent. As the solvent, it is not particularly limited. Silicone polymer is obtained by appropriately blending and agitating silane compound, catalyst, water and solvent. At this time, the concentration of the silane compound, the temperature of reaction, the reaction time period and the like are not particularly limited.

[0015]

These silicone polymers cover the surface of the metal hydrate and enhances the temperature at which the metal hydrate releases the water held by itself. Usually, the temperature at which the metal hydrate releases water, can be measured by loss of heating method, differential scanning calorimeter or thermal decomposition gas chromatography from the metal hydrate. The temperatures at which it releases water are largely different depending on the kinds, shapes and the like of the metal hydrates. If aluminium hydroxide is used as a metal hydrate, by processing with the above-described silicone polymer, the temperature becomes higher by a few °C to a few of tens °C.

[0016]

Moreover, in the present invention, a variety of coupling agents or the like besides silicone polymers may be used in combination. As a coupling agent, silane based coupling agent, titanate based coupling agent and the like are listed. As a silane based coupling agent, in general, epoxy silane based coupling agent, amino silane based coupling agent, cationic silane based coupling agent, vinyl silane based coupling agent, acryl silane based coupling agent, mercapto silane based coupling agent, their composite based coupling agent and the like are listed. The blending ratios in the cases of using the various coupling agents in combination are not particularly limited but, in order to exhibit both the characteristics, it is preferable that the weight ratio of the coupling agent and the silicone polymer is made in the range of 0.001:1 to 1:0.001. Moreover, it is particularly preferable that it is made in the range of 0.001:1 to 1:1.

[0017]

The resin material used in the present invention is not particularly limited, but provided that it does not contain bromine. As a resin material, for example, an epoxy resin, a polyimide resin, a triazine resin, a phenol resin, a melamine resin, their denatured substances of these resins and the like are used. Moreover, as to these resins, more than two kinds of these may be used in combination, a variety of hardening agents, hardening accelerators and the like may be added according to the necessity, and these may be also blended as solvent solution. The blending volume is determined by the ratio with respect to the volume of inorganic filler containing a metal hydrate. It is preferable that the total blending volume of the hardening agent and hardening accelerator used according to the resin and the necessity is in the range of 20% by weight to 80% by weight of the total solids of the resin composition. As epoxy resin, for example, a bisphenol type epoxy resin, a novolac type epoxy resin, alicyclic epoxy resin, an epoxylated polybutadiene, a glycidyl ester type epoxy resin

and a glycidylamine type epoxy resin are preferably used. Specifically, a bisphenol type epoxy resin such as a bisphenol A type epoxy resin, a bisphenol F type epoxy resin and a bisphenol S type epoxy resin, a novolac type epoxy resin such as a cesol novolac type epoxy resin, a bisphenol A novolac type epoxy resin, a salicylaldehyde novolac type epoxy resin are more preferably used. Considering the improvement of heat resistance, a bisphenol A novolac type epoxy resin, a cresol novolac type epoxy resin, or a salicylaldehyde phenol novolac type epoxy resin is particularly preferable. The resin may be used alone, or more than two kinds may be used.

[0018]

As a hardening agent, a variety of conventionally known kinds can be used. For example, if an epoxy resin is used as a resin, a hardening agent for use is, for example, multifunctional phenol such as dicyandiamide, diaminodiphenylmethane, diaminodiphenyl sulfone, phthalic anhydride, pyromellitic anhydride, phenol novolak and cresol novolak. For these hardening agents, several kinds of these can be also used in combination. The kinds of hardening accelerators and blending volumes are not particularly limited, for example, imidazole based compound, organic phosphorus based compound, the tertiary amine, the quaternary ammonium salt are used or the two kinds or more of these may be used in combination.

[0019]

A solvent is often used in order to dilute these resin materials, metal hydrates, silicone polymers and the like to be varnished. This solvent is not particularly limited, but, for example, acetone, methyl ethyl ketone, toluene, xylene, methyl isobutyl ketone, ethyl acetate, ethylene glycol mono methyl ether, N, N-dimethyl formamide, methanol and ethanol are listed. These solvents may be used singly or may be blended with several kinds. Moreover, the solid concentration of varnish is not limited, and can be appropriately changed depending upon the resin compositions, and the kinds and the blending volume and the like of the inorganic fillers. However,



it is preferable that it is in the range of 50% by weight to 85% by weight. When the solid is lower than 50% by weight, there is a tendency that the varnish viscosity is lower and the resin portion of the prepreg is too low. Moreover, if the solid is higher than 85% by weight, there is a tendency that the appearance of the prepreg, and the like are significantly lowered due to the increased viscosity of the varnish and the like.

[0020]

The methods of processing the surface of the metal hydrate at the time of varnishing are not particularly limited: the metal hydrate in which the above-described silicone polymer has been previously processed may be used; a silicone polymer may be blended with a resin and a metal hydrate at the time of varnishing; or the varnishing may be performed as it is after the metal hydrate is inputted into the processing liquid into which the silicone polymer and the like have been previously inputted and the agitation processing has been carried out.

[0021]

A prepreg for a printed wiring board is obtained by blending the respective components to obtain a varnish, impregnating obtained varnish into the base material and drying in the range of 80°C to 200°C in the drying furnace. As a base material, if it is used at the time of manufacturing a metal foil-clad laminated plate and a multilayer printed wiring board, it is not particularly limited, but usually fiber base materials such as a woven fabric and a nonwoven fabric are used. As a fiber base material, for example, inorganic fibers such as glass, alumina, asbestos, boron, silica alumina glass, silica glass, Si-Ti-C-O fiber reinforced SiC {chirano fiber}, silicon carbide, silicon nitride, zirconium, and organic fibers such as aramid, polyether ether ketone, polyether imide, polyether sulfone, carbon, cellulose and the like are listed. These may be used singly or the two kinds or more of these may be used in combination. As a fiber base material, the woven fabric of glass fiber is particularly preferable.

[0022]

A laminated plate can be prepared by lapping sheets of the such-obtained prepreg according to the thickness of the laminated plate to be manufactured, and by heating and applying a pressure. It may be used along with the other prepreg in combination. Considering that the laminated surface contacts with the flame, it is preferable that a prepreg of the present invention with incombustibility is applied to the surface layer. A metal-clad laminated plate is manufactured by lapping a metal foil on the prepreg, heating and pressurizing at 150°C to 200°C, in the range of 1.0 Mpa to 8.0 Mpa. As a metal foil, it is not particularly limited, but the copper foil is preferably used from the electrical and economical viewpoints. A printed wiring board can be obtained by using a method usually used such as a subtract method, perforating and the like.

[0023]

The prepreg, the metal laminated plate and the printed wiring board of the present invention can be used as a material of the multi-layer wiring board.

[0024]

According to the present invention, the laminated plate is manufactured by employing the metal hydrate and the silicone polymer in combination, an incombustibility can be manufactured although bromine compound is not used, and the decreasing in the heat resistance occurred by blending the metal hydrate is capable of being suppressed.

[0025]

[Preferred Embodiments]

Hereinafter, examples of the present invention will be described.

[0026]

(Example 1)

40g of tetramethoxy silane and 93g of methanol were blended in a glass flask equipped with an agitator, a condenser and a thermometer to obtain a solution. To the obtained solution, 0.47g of acetic acid and 18.9g of distilled water were

added and stirred at 50°C for 8 hours to synthesize a silicone polymer. The average degree of polymerization of the obtained silicone polymer was 20. It should be noted that the average degree of polymerization was calculated from the number average molecular weight measured by utilizing a calibration curve of standard polystyrene by gel permeation chromatography. To the obtained oligomer, methylethyl ketone was added to prepare a silicon oligomer solution having 25% by weight of solids.

As indicated below, a resin, a metal hydrate and methylethyl ketone were blended to the obtained silicone polymer solution, to prepare a varnish having 70% by weight of solids.

Bisphenol A type epoxy resin (Ep1001 made by Oil Chemical Shell Epoxy, Co., Ltd.; epoxy equivalent: 466)

30 parts by weight

Orthocresol novolak type epoxy resin (ESCN-195 made by Sumitomo Chemical, Co., Ltd.; epoxy equivalent: 195)

70 parts by weight

Dicyan diamide

5 parts by weight

2-ethyl-4-methyl imidazole 0.5 parts by weight

aluminium hydroxide (CL310 made by Sumitomo Chemical, Co., Ltd.)

155 parts by weight

Silicone polymer solution (25% by weight)

4 parts by weight

[0027]

(Example 2)

As similarly to Example 1, 40g of trimethoxymethyl silane and 93g of methanol were blended to obtain a solution. To the obtained solution, 0.53g of acetic acid and 15.8g of distilled water were added and then stirred at 50°C for 8 hours to synthesize a silicone polymer. The average degree of polymerization of the obtained silicone polymer was 15. To the obtained silicone polymer, methylethyl ketone was added to prepare a silicone polymer solution having 25% by weight of solids. A varnish was prepared similarly to Example 1, by employing the obtained silicone polymer solution.

[0028]

(Example 3)

As similarly to Example 1, 20g of dimethoxydimethyl silane, 25g of tetramethoxy silane and 105g of methanol were blended to obtain a solution. To the obtained solution, 0.60g of acetic acid and 17.8g of distilled water were added and stirred at 50°C for 8 hours to synthesize a silicone polymer. The average degree of polymerization of the obtained silicone polymer was 30. To the obtained silicone polymer, methylethyl ketone was added to prepare a silicone polymer solution having 25% by weight of solids. A varnish was prepared similarly to Example 1, by employing the obtained silicone polymer solution.

[0029]

(Example 4)

As similarly to Example 1, 20g of trimethoxymethyl silane, 22g of tetramethoxy silane and 98g of methanol were blended to obtain a solution. To the obtained solution, 0.52g of acetic acid and 18.3g of distilled water were added and then stirred at 50°C for 8 hours to synthesize a silicone polymer. The average degree of polymerization of the obtained silicone polymer was 25. To the obtained silicone polymer, methylethyl ketone was added to prepare a silicone polymer solution having 25% by weight of solids. A varnish was prepared similarly to Example 1, by employing the obtained silicone polymer solution.

[0030]

(Example 5)

As similarly to Example 1, 10g of dimethoxydimethyl silane, 10g of trimethoxymethyl silane, 20g of tetramethoxy silane and 93g of methanol were blended to obtain a solution. To the obtained solution, 0.52g of acetic acid and 16.5g of distilled water were added and then stirred at 50°C for 8 hours to synthesize a silicone polymer. The average degree of polymerization of the obtained silicone polymer was 23. To the obtained silicone polymer, methylethyl ketone was added to prepare a silicone polymer solution having 25% by weight of solids. A varnish was prepared similarly to Example 1, by

employing the obtained silicone polymer solution.

[0031]

(Example 6)

As similarly to Example 1, 40g of tetraethoxy silane and 93g of methanol were blended to obtain a solution. To the obtained solution, 0.34g of acetic acid and 13.8g of distilled water were added and then stirred at 50°C for 8 hours to synthesize a silicone polymer. The average degree of polymerization of the obtained silicone polymer was 19. To the obtained silicone polymer, methylethyl ketone was added to prepare a silicone polymer solution having 25% by weight of solids. A varnish was prepared similarly to Example 1, by employing the obtained silicone polymer solution.

[0032]

(Example 7)

As similarly to Example 1, 40g of diphenyldimethoxy silane and 10g of methanol were blended to obtain a solution. To the obtained solution, 0.20g of acetic acid and 6.0g of distilled water were added and then stirred at 25°C for 1 hour to synthesize a silicone polymer. The average degree of polymerization of the obtained silicone polymer was 2. To the obtained silicone polymer, methylethyl ketone was added to prepare a silicone polymer solution having 25% by weight of solids. A varnish was prepared similarly to Example 1, by employing the obtained silicone polymer solution.

[0033]

(Example 8)

As similarly to Example 1, 40g of diphenyldimethoxy silane and 10g of methanol were blended to obtain a solution. To the obtained solution, 0.20g of acetic acid and 6.0g of distilled water were added and then stirred at 50°C for 8 hours to synthesize a silicone polymer. The average degree of polymerization of the obtained silicone polymer was 8. To the obtained silicone polymer, methylethyl ketone was added to prepare a silicone polymer solution having 25% by weight of solids. A varnish was prepared similarly to Example 1, by

employing the obtained silicone polymer solution.

[0034]

(Example 9)

As similarly to Example 1, 40g of phenyltrimethoxy silane and 10g of methanol were blended to obtain a solution. To the obtained solution, 0.24g of acetic acid and 11.0g of distilled water were added and then stirred at 50°C for 8 hours to synthesize a silicone polymer. The average degree of polymerization of the obtained silicone polymer was 12. To the obtained silicone polymer, methylethyl ketone was added to prepare a silicone polymer solution having 25% by weight of solids. A varnish was prepared similarly to Example 1, by employing the obtained silicone polymer solution.

[0035]

(Example 10)

As similarly to Example 1, 40g of diphenyldimethoxy silane and 10g of methanol were blended to obtain a solution. To the obtained solution, 0.18g of acetic acid and 5.5g of distilled water were added and then stirred at 50°C for 8 hours to synthesize a silicone polymer. The average degree of polymerization of the obtained silicone polymer was 10. To the obtained silicone polymer, methylethyl ketone was added to prepare a silicone polymer solution having 25% by weight of solids. A varnish was prepared similarly to Example 1, by employing the obtained silicone polymer solution.

[0036]

(Example 11)

As similarly to Example 1, 40g of phenyltriethoxy silane and 10g of methanol were blended to obtain a solution. To the obtained solution, 0.20g of acetic acid and 9.0g of distilled water were added and then stirred at 50°C for 8 hours to synthesize a silicone polymer. The average degree of polymerization of the obtained silicone polymer was 9. To the obtained silicone polymer, methylethyl ketone was added to prepare a silicone polymer solution having 25% by weight of solids. A varnish was prepared similarly to Example 1, by

employing the obtained silicone polymer solution.

[0037]

(Example 12)

As similarly to Example 1, 20g of diphenyldimethoxy silane, 20g of tetramethoxy silane and 10g of methanol were blended to obtain a solution. To the obtained solution, 0.25g of acetic acid and 12.5g of distilled water were added and then stirred at 50°C for 8 hours to synthesize a silicone polymer. The average degree of polymerization of the obtained silicone polymer was 15. To the obtained silicone polymer, methylethyl ketone was added to prepare a silicone polymer solution having 25% by weight of solids. A varnish was prepared similarly to Example 1, by employing the obtained silicone polymer solution.

[0038]

(Example 13)

As similarly to Example 1, 20g of diphenyldimethoxy silane, 20g of dimethoxydimethyl silane and 10g of methanol were blended to obtain a solution. To the obtained solution, 0.28g of acetic acid and 9.0g of distilled water were added and then stirred at 50°C for 8 hours to synthesize a silicone polymer. The average degree of polymerization of the obtained silicone polymer was 8. To the obtained silicone polymer, methylethyl ketone was added to prepare a silicone polymer solution having 25% by weight of solids. A varnish was prepared similarly to Example 1, by employing the obtained silicone polymer solution.

[0039]

(Example 14)

As similarly to Example 1, 20g of diphenyldimethoxy silane, 20g of trimethoxymethyl silane and 10g of methanol were blended to obtain a solution. To the obtained solution, 0.25g of acetic acid and 11.0g of distilled water were added and then stirred at 50°C for 8 hours to synthesize a silicone polymer. The average degree of polymerization of the obtained silicone polymer was 10. To the obtained silicone polymer, methylethyl ketone was added to prepare a silicone polymer solution having 25% by weight of solids. A varnish was prepared similarly to

Example 1, by employing the obtained silicone polymer solution.

[0040]

(Example 15)

As similarly to Example 1, 20g of diphenyldimethoxy silane, 20g of phenyltrimethoxy silane and 10g of methanol were blended to obtain a solution. To the obtained solution, 0.30g of acetic acid and 5.9g of distilled water were added and then stirred at 50°C for 8 hours to synthesize a silicone polymer. The average degree of polymerization of the obtained silicone polymer was 6. To the obtained silicone polymer, methylethyl ketone was added to prepare a silicone polymer solution having 25% by weight of solids. A varnish was prepared similarly to Example 1, by employing the obtained silicone polymer solution.

[0041]

(Example 16)

To the silicone polymer synthesized solution obtained in Example 7,  $\gamma$ -glycidoxypropyl trimethoxysilane (product name: A-187 made by Nippon Unicar, Co., Ltd.) as silane coupling agent and methylethyl ketone were added, in the ratio of 50:50 (weight ratio) to prepare a silicone polymer/silane coupling agent solution having 25% by weight of solids. A varnish was prepared similarly to Example 1 by employing the obtained silicone polymer/silane coupling agent solution in place of the silicone polymer solution of Example 1.

[0042]

(Example 17)

To the silicone polymer solution obtained in Example 7, isopropyl tris (dioctylpyrophosphate) titanate (product name: KR46B made by Ajinomoto, Co., Inc) as titanate coupling agents and methylethyl ketone were added, in the ratio of 50:50 (weight ratio) to prepare a silicone polymer/silane coupling agent solution having 25% by weight of solids. A varnish was prepared similarly to Example 1 by employing the obtained silicone polymer/silane coupling agent solution in place of the silicone polymer solution of Example 1.

[0043]



(Example 18)

A varnish was prepared similarly to Example 7 except that magnesium hydroxide was used in place of aluminium hydroxide as a metal hydrate.

[0044]

(Example 19)

A varnish was prepared similarly to Example 7 except that calcium hydroxide was used in place of aluminium hydroxide as a metal hydrate.

[0045]

(Example 20)

A varnish was prepared similarly to Example 7 except that 100 parts by weight of aluminium hydroxide and 55 parts by weight of magnesium hydroxide were used as metal hydrates.

[0046]

(Example 21)

A varnish was prepared similarly to Example 7 except that 100 parts by weight of orthocresol novolak type epoxy resin as an epoxy resin (ESCN-195 made by Sumitomo Chemical; epoxy equivalent: 195) and 55 parts by weight of phenol novolak resin (HP-850N made by Hitachi Chemical, Co., Ltd.; hydroxyl group equivalent: 108) in place of dicyandiamide were used.

[0047]

(Example 22)

A varnish was prepared similarly to Example 7 except that the blending volume of aluminium hydroxide was 230 parts by weight.

[0048]

(Example 23)

To the silicone polymer obtained in Example 7, methanol was added to prepare a silicone polymer processing solution having 3% by weight of solids. To the obtained processing solution, the same volume of aluminium hydroxide with that of Example 21 was added and stirred at 25°C for 1 hour, and then dried at 80°C for 3 hours to prepare a silicone polymer processing aluminium hydroxide. A varnish was prepared

similarly to Example 21, by employing the obtained processed aluminium hydroxide.

[0049]

(Example 24)

To the silicone polymer obtained in Example 7, methylethyl ketone was added to prepare a silicone polymer processing solution having 5% by weight of solids. To the obtained processing solution, the same volume of aluminium hydroxide as that of Example 21 was added and stirred at 25°C for 1 hour to obtain a processing solution, and then employing the solution to prepare a varnish similarly to Example 21.

[0050]

(Comparative Example 1)

A varnish was prepared without blending a silicone polymer solution to the varnish of Example 1.

[0051]

(Comparative Example 2)

A varnish was prepared similarly to Example 1 except that 1 part by weight of  $\gamma$ -glycidoxypropyl trimethoxysilane (product name: A-187 made by Nippon Unicar, Co., Ltd.) was used in place of the silicone polymer of Example 1.

[0052]

(Comparative Example 3)

A varnish was prepared similarly to Example 1 except that 1 part by weight of isopropyl tris (dioctylpyro phosphate) titanate (product name: KR46B made by Ajinomoto, Co., Ltd.) was used in place of the silicone polymer of Example 1.

[0053]

(Comparative Example 4)

A varnish was prepared similarly to Example 7 except that 1 part by weight of diphenyldimethoxy silane compound was blended in place of the silicone polymer of Example 7.

[0054]

(Comparative Example 5)

A varnish was prepared by changing from 155 weight portions of aluminium hydroxide of the varnish in Example 1,

to 20 weight portions of the same.

[0055]

The varnishes prepared in Examples 1 to 24 and Comparative Examples 1 to 5 were impregnated into a glass fabric (#2116, E-glass) with a thickness of about 0.1 mm, and then heated and dried at 150°C for 3 to 10 minutes, to obtain prepregs having 43% by weight of resin. Four obtained prepregs were piled and a copper foil with a thickness of 18  $\mu$ m was placed on both sides on the piled prepregs, and then pressed at 170°C for 90 minutes at 4.0 Mpa to manufacture a both sides copper-clad laminated plate respectively.

[0056]

The obtained both sides copper-clad laminated plates were evaluated from the viewpoints of the incombustibility and the heat resistance. The results are indicated in Table 1 through Table 4.

The methods of testing are as follows:

Incombustibility: by using a laminated plate on which the whole surface is etched, evaluated by the vertical test in conformity with the UL 94 standards.

Heat resistance: measured the time period until the laminated plate was swollen after the laminated plate floated on the melted solder at 260°C and 288°C respectively, using both sides copper-clad laminated plate cut in the size of 50 mm x 50 mm.

[Table 1]

Item		Example 1	Example 2	Example 3	Example 4
Incombustibility (S)	Max.	7.0	8.3	8.0	8.5
	Av.	4.6	4.9	4.9	4.7
Heat resistance (S, float)	260°C	>300	>300	>300	>300
	288°C	>300	>300	>300	>300

Item		Example 5	Example 6	Example 7	Example 8
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Incombustibility (S)	Max.	8.2	7.6	4.8	3.9
	Av.	4.0	4.8	3.3	2.4
Heat resistance (S, float)	260°C	>300	>300	>300	>300
	288°C	>300	>300	>300	>300

[Table 2]

Item		Example 9	Example 10	Example 11	Example 12
Incombustibility (S)	Max.	5.0	5.1	6.0	5.5
	Av.	4.2	3.0	4.3	3.9
Heat resistance (S, float)	260°C	>300	>300	>300	>300
	288°C	>300	>300	>300	>300

Item		Example 13	Example 14	Example 15	Example 16
Incombustibility (S)	Max.	6.5	6.0	6.3	4.9
	Av.	4.5	4.1	4.2	2.8
Heat resistance (S, float)	260°C	>300	>300	>300	>300
	288°C	>300	>300	>300	>300

[Table 3]

Item		Example 17	Example 18	Example 19	Example 20
Incombustibility (S)	Max.	5.0	4.0	7.5	4.3
	Av.	3.0	2.2	4.9	2.9
Heat resistance (S, float)	260°C	>300	>300	>300	>300
	288°C	>300	>300	>300	>300

Item		Example 21	Example 22	Example 23	Example 24
Incombustibility (S)	Max.	4.1	3.0	4.6	4.1
	Av.	2.8	1.5	3.0	2.6
Heat resistance (S, float)	260°C	>300	>300	>300	>300
	288°C	>300	>300	>300	>300

[Table 4]

Item		Comparative Example 1	Comparative Example 2	Comparative Example 3
Incombustibility (S)	Max.	15.5	13.6	14.8
	Av.	8.6	8.3	9.0
Heat resistance (S, float)	260°C	150	180	144
	288°C	25	47	39

Item		Comparative Example 4	Comparative Example 5
Incombustibility (S)	Max.	11.5	Burned up
	Av.	6.0	Burned up
Heat resistance (S, float)	260°C	193	>300
	288°C	55	>300

[0057]

From the above-described results, it is considered that Examples 1 through 24 achieve the UL 94V-0 standard, and their heat resistances at 260°C and their heat resistances at 288°C are fairly good.

[0058]

#### [EFFECTS OF THE INVENTION]

The resin composition of the present invention is used, thereby manufacturing the prepreg, laminated plate, metal-clad laminated plate, printed wiring board, multiplayer wiring board, and the like which have lately been desired, manifest the superior incombustibility without requiring a material containing bromine, and realize the high heat-resistance.